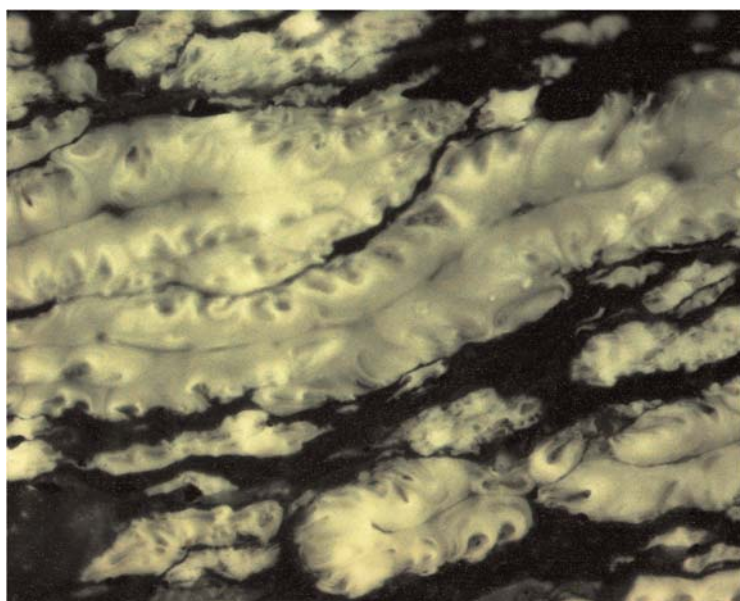


Analytical methods

Petroleum exploration



The geochemical laboratory of TNO (Geolab) is one of the biggest geochemical facilities of its kind in Europe, maybe even in the world.

An overview is given of the analytical methods that are available at the Geolab to collect organic geochemical data for, among others, source rock characterisation and oil-source rock correlation.

- 1 Carbon and sulfur analysis (Leco CS)
- 2 Rock Eval VI analysis
- 3 Vitrinite reflectance measurements
- 4 Extraction and fractionation
- 5 Gas Chromatography Mass Spectrometry (GC-MS)
- 6 Gas Chromatography Isotope Ratio Mass Spectrometry (GC-IRMS)

1 Carbon and sulfur (Leco CS)

Total carbon and sulfur are measured with a LECO SC 144DR. The total carbon content is analysed by total combustion of 0.2 - 0.3 gram of sample at 1350 °C while detecting the evolving CO₂ and SO₂ by means of an infrared-detector. The amount of CO₂ and SO₂ is calibrated with a pure calcite standard and pure Ag₂SO₄, respectively. Relative standard deviations are less than 5%.

After the initial CS analysis, the total organic carbon content is determined on a selection of samples by measuring the sample after decalcifying with 1N HCl on a hotplate. About 0.2 - 0.3 gram of sample is weighed

into a ceramic sample boat. The sample is placed on a hot plate at 90 °C and about 15 drops of HCl are added. After the sample is dry, a second aliquot of HCl is added to the sample. If there is still any visible reaction of the HCl with carbonates within the sample, the procedure is repeated.

Quality control (QC) standards are analysed at the beginning and at the end of each analytical run and after every 20 unknown samples. QC charting and verification are carried out using Shewhart (1931) control charts constructed in Microsoft Excel, onto which are plotted the mean and standard deviation of the QC data.



2 Rock Eval VI

The results of a Rock Eval analysis are used to evaluate rapidly the petroleum-generating potential of rocks, and it provides information on the quantity, type, and thermal maturity of the organic matter in a potential source rock.

Successful petroleum exploration relies on detailed analysis of the petroleum system in a given area. Identification of potential source rocks, their maturity and kinetic parameters, and their regional distribution are best accomplished by rapid screening of rock samples (cores and/or cuttings) using the Rock-Eval apparatus. The technique has been routinely used for about fifteen years and has become a standard tool for hydrocarbon exploration.

At the laboratory of TNO a Rock Eval VI plus TOC module is used. Samples chosen to be measured on the Rock Eval are usually subsampled from material previously crushed for analyses on a Leco CS.



The Rock Eval has a wide spectrum of applications:

- source rock characterization,
- reservoir geochemistry,
- environmental studies

3 Organic petrology

Organic petrology is the study of the composition, characteristics, origin and distribution of sedimentary organic matter, including coal deposits. In petroleum exploration, organic petrology is a key discipline in assessing prospectivity, largely

through the assessment of the generation potential of source rocks, including the analysis of organic facies (maceral composition) and the determination of the thermal maturity (vitrinite reflectance). Organic petrological data are used as fundamental inputs into basin models to assess the amounts and timing of petroleum generation and expulsion.

Aspects of organic petrology have found many applications in fundamental and applied earth sciences. Vitrinite reflectance measurements for example, are commonly used in petroleum exploration, coal rank determination, basin modeling, and minerals exploration. Maceral analysis is used in petroleum source rock characterization, blending of coals for coke-making, and interpretation of paleodepositional environments.

The geochemical laboratory of TNO is equipped to do petrographic analyses of organic and associated components of oils, coals and potential petroleum source rocks.

The core instrument for organic petrological research is a fully dedicated microscope for vitrinite reflectance measurements and maceral analyses. The instrument consists of a Leica motorized DMLA microscope equipped with a xyz-stage and a digital Basler video camera. The digital camera shows the live image on screen in full resolution and the vitrinite reflectance measurements can be carried out at any position of the image. Maceral analyses can be carried on this system according to the classical point counting method.

4 Solvent extraction and fractionation

The fraction of the organic matter that is soluble in organic solutes is extracted from the powdered samples (10 - 20 g) by soxhlett extraction with dichloromethane (DCM) and methanol (MeOH) (95:5 v.v.) for 24 hours. The solvent is evaporated by careful rotary evaporation and, after transfer of the liquid extract into small vials, by air drying in the

fume hut. After these steps the mass of the extractable organic matter (EOM) is determined.

The extract contains next to aliphatic-, aromatic- and NSO-components an amount of asphaltenes, which have to be removed from the extract prior to the GC-MS analysis.

The extract is separated in four hydrocarbon-groups using a flash-column. The stationary phase in this column is silica gel, which was activated for 1 hour at 150 °C.

Three fractions - aliphatic, aromatic, and NSO-components - are eluted with respectively n-pentane, dichloromethane and methanol. The asphaltenes fraction is not dissolved and remains on the column.

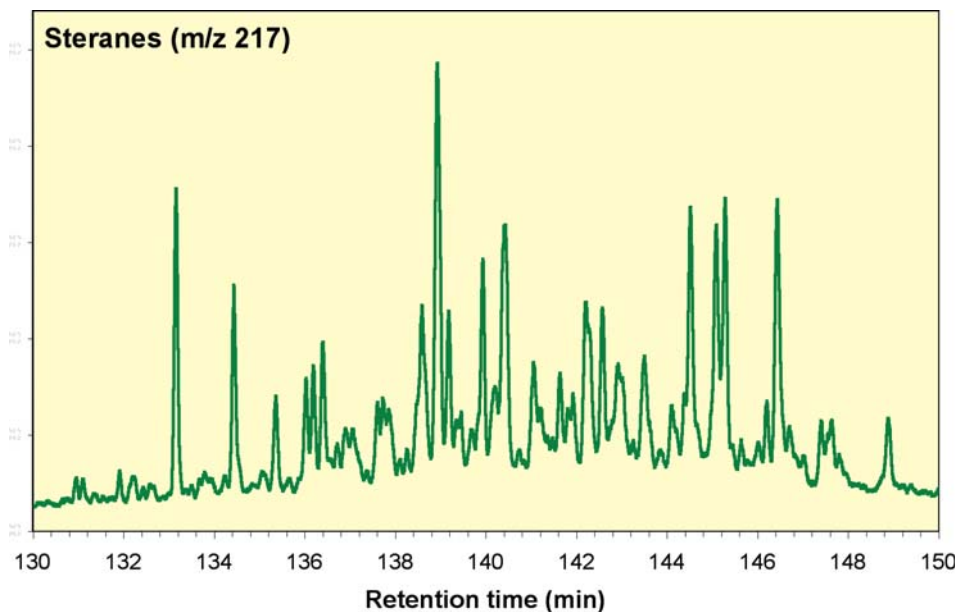
The mass of each fraction is determined. The fractions are diluted with n-pentane ($c = 1 \text{ mg/mL}$) and analysed by GC-MS or GC-IRMS.

5 Gas Chromatography Mass spectrometry (GC-MS)

Mass spectrometry is used to identify unknown compounds and quantify known compounds. It is sensitive and selective and is commonly used in combination with a separation technique, such as gas or liquid chromatography, to analyze complex mixtures. After a molecule is introduced into the mass spectrometer, the molecule is first ionized, then fragmented. Following this, the ions can be selected and counted. The plot of the mass-to-charge ratio (m/z) of these ions, as a function of abundance, is a mass spectrum.

A quadrupole mass filter can be operated in a scan mode (TIC) or select ion monitoring (SIM) mode.

In SIM, the mass filter is set to pass one selected m/z . This provides the greatest sensitivity and is used for quantitative applications (biomarker analysis). It is used when the analyst has prior knowledge of what ions to expect. In scan mode, the mass filter is set to sequentially pass a range of masses. It has lower sensitivity because most of the ions strike the rods during the scan,



The ratio of these isotopes in natural materials varies slightly as a result of isotopic fractionation during physical, chemical and biological processes resulting, in some cases, with the relative isotopic ratio of specific compounds being highly diagnostic of key environmental processes. The primary prerequisite for GC-IRMS is that the compounds constituting the sample mixture are amenable to GC, i.e. they are suitably volatile and thermally stable. In hydrocarbon exploration studies compound specific carbon and hydrogen isotope ratio's of individual n-alkanes are primarily used for the characterisation of source rock extracts, condensates and oil samples. These data are used for, among others, oil-source rock correlations.

generating a Total Ion Current (TIC). For general unknowns, the selected mass may be at 100, then 101, then 102 and so on. This mode is used to collect spectra for interpretation or a library search. When a sample contains several components, they may be separated (in time) using chromatographic techniques. After each component enters the mass spectrometer, its molecules are ionized, filtered, and detected to produce a unique mass spectrum. The individual spectra are used to identify the components.

The data from a GC-MS analysis are used, among others, for the characterisation of hydrocarbons in terms of maturity and facies of the original source rock. Biomarker data (e.g. steranes and terpanes) are used in oil-source rock correlations.

6 Gas Chromatography – Isotope Ratio Mass Spectrometry (GC-IRMS)

Gas chromatography isotope ratio mass spectrometry (GC-IRMS) is a highly specialised instrumental technique used to ascertain the relative ratio of light stable isotopes of carbon ($^{13}\text{C}/^{12}\text{C}$), hydrogen ($^2\text{H}/^1\text{H}$), nitrogen ($^{15}\text{N}/^{14}\text{N}$) or oxygen ($^{18}\text{O}/^{16}\text{O}$) in individual compounds separated from often complex mixtures of components.



Quality assurance

In order to guarantee data quality and integrity each analysis is performed according to a standard operating procedure (SOP). These procedures are an integral part of the Quality Assurance (QA) manual of the geochemical laboratory of TNO.

Quality control (QC) practices consist of more focused, routine, day-to-day activities carried out within the scope of the overall QA program. QC is the routine application of procedures for obtaining data that are accurate (precise and unbiased), representative, comparable, and complete. QC procedures include activities such as identification of sampling and analytical methods, calibration and standardisation, and sample custody and record keeping. Audits, reviews, and complete and thorough documentation are used to verify compliance with predefined QC procedures.

Contact

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Geobiology

TNO Built Environment and Geosciences *Geological Survey of the Netherlands* is the central geoscience centre in the Netherlands for information and research to promote the sustainable management and use of the subsurface and its natural resources.

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